

# Characterization of a Nylon 6/Poly(methyl Acrylate) Copolymer Produced by Radiation Grafting

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## Synopsis

Acrylic acid has been grafted onto nylon 6 by the mutual  $\gamma$ -irradiation technique. Methods are described for removing poly(acrylic acid) homopolymer and ungrafted nylon, the latter involving intermediate conversion to the calcium ionomer. The pure graft copolymer in its methylated form, viz., nylon 6/poly(methyl acrylate), NY/PMA, was characterized by light scattering in mixed solvents to yield the true molecular weight ( $3.2 \times 10^6$ ) as well as the molecular weights  $M_{\text{PMA}}(\text{domain})$  and  $M_{\text{NY}}(\text{domain})$  of the PMA and NY portions, respectively. The molecular weight  $M_{\text{PMA}}$  of the grafts was measured after hydrolysis of the backbone, and the molecular weight  $M_{\text{NY}}$  of the backbone was determined via a previously devised indirect procedure. Comparisons of  $M_{\text{PMA}}(\text{domain})$  with  $M_{\text{PMA}}$  and of  $M_{\text{NY}}(\text{domain})$  with  $M_{\text{NY}}$  gave  $\sim 7$  nylon chains and  $\sim 17$  poly(methyl acrylate) chains per copolymer molecule. Chain transfer and bimolecular termination during grafting are proposed as probable contributory factors to the branched structure of the copolymer.

## INTRODUCTION

A previous communication was devoted to solution properties of nylon 6 and poly(methyl acrylate) in mixed solvents.<sup>1</sup> It was indicated therein that the findings were intended as an adjunct to the subsequent characterization of a copolymer comprising these two polymers. The results of this characterization form the basis of the present work.

Copolymers prepared via radiation grafting present two unusual features. First, they comprise a large proportion of ungrafted material so that the apparent degree of grafting is often much less than the true one. Secondly, because of selective grafting to longer chains within the initially heterogeneous polymer, the molecular weight of the backbone in the pure copolymer is greater than that of the initial polymer.<sup>2</sup> It is the purpose of this study to allow for these factors by careful attention to extraction when obtaining the pure copolymer, as well as to the determination of the weight fraction of initial nylon 6 which participates in grafting. The latter enters into the indirect determination of the molecular weight of the nylon backbone in the copolymer.<sup>2</sup>

Prior to measurements on the copolymer and isolated grafts, methylation of the carboxyl groups in the poly(acrylic acid) was effected in order to extend the range of solvents and obviate possible polyelectrolyte behavior. The following abbreviations are adopted: AA, acrylic acid;  $M$ , relative molar mass; NY, nylon 6; OCP, *o*-chlorophenol; PAA, poly(acrylic acid); PACa, poly(calcium acrylate); PANa, poly(sodium acrylate); PMA, poly(methyl acrylate); TFP, 2,2,3,3-tetrafluoropropanol.

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## EXPERIMENTAL

## Preparation of Copolymer

The procedures involved in the preparation of the copolymer, isolation of the grafts, and removal of ungrafted nylon 6 (NY) are indicated schematically in Figure 1. The following experimental details relate to stages (a) through (k) in this figure.

Films of NY were immersed in an aqueous solution comprising  $[AA] = 10\%$  v/v ( $\approx 1.46 \text{ mole/dm}^3$ ) and  $[CuCl_2] = 1 \times 10^{-3} \text{ mole/dm}^3$ . The purpose of the  $CuCl_2$  was to suppress partially the otherwise excessive homopolymerization. After several freeze-thaw cycles, the ampoules were sealed ( $6.6 \times 10^{-3} \text{ N/m}^2$  pressure) and subjected to  $\gamma$ -irradiation from a  $^{60}Co$  source [stage (a)]. The dose rate, irradiation time, and temperature were 3.1 mW/kg, 8 hr, and 303 K, respectively.

Unreacted AA and occluded PAA homopolymer were removed from grafted films by two separate washings with hot deionized water, followed by Soxhlet extraction with water for 24 hr [stage (b)]. Films were dried between glass plates for seven days under vacuum at 313 K, a portion then being subjected to stages (c) and (d) and the remainder being treated via stage (e) and following stages. In stage (c) the mixture of grafted and ungrafted NY was hydrolyzed with HCl, the breakdown products being dialyzed off leaving a solution of the PAA grafts. This was methylated with diazomethane solution in stage (d) according to a previously described procedure.<sup>2</sup>

To facilitate subsequent reactions, the mixture of grafted and ungrafted NY was converted to a powdery form by dissolving the films in aqueous 98% formic acid followed by precipitation in cold deionized water [stage (e)]. The precipitate was centrifuged and washed several times with water. Aqueous  $Na_2CO_3$  (10% w/v) was added and the mixture was stirred overnight at 333 K [stage (f)]. Excess

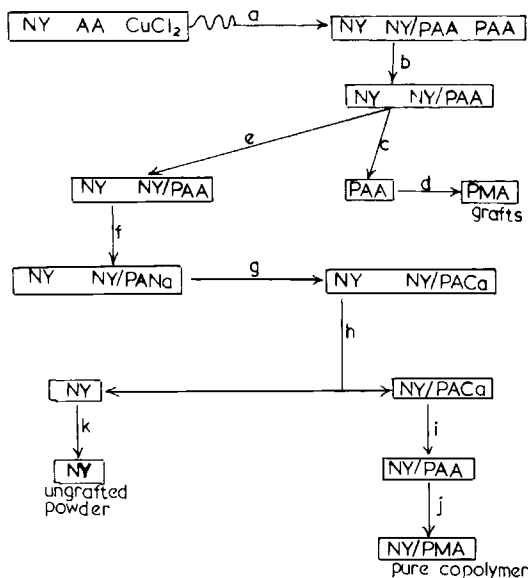


Fig. 1. Reaction scheme for preparation of pure graft copolymer, isolation of ungrafted nylon and isolation of grafts.

of  $\text{Na}_2\text{CO}_3$  was removed by repeated aqueous washings and centrifugations. Aqueous calcium acetate (10% w/v) was added to the precipitate, and the mixture was stirred overnight at 333 K [stage (g)]. The excess of calcium acetate was removed in the same way as that used for removal of excess of  $\text{Na}_2\text{CO}_3$ . The precipitate was dried under vacuum at 313 K to yield a white powder comprised of ungrafted NY and graft copolymer with the grafts in the form of PACa. In this form there is partial crosslinking via bivalent  $\text{Ca}^{2+}$  ions. This increases the resistance of the graft copolymer to dissolution and thus facilitates removal of any ungrafted NY by means of a suitable solvent (*m*-cresol).

The precipitate was stirred vigorously with *m*-cresol for 24 hr at 353 K [stage (h)] before being centrifuged. The supernatant solution of extracted NY was decanted off, fresh *m*-cresol was added, and heating with stirring was repeated for 24 hr. The undissolved residue, NY/PACa, was washed with acetone and centrifuged several times before drying. Regeneration of the grafts in the pure copolymer to their acid form was accomplished by stirring the solid with 10% (w/v) aqueous acetic acid for 24 hr at 333 K [stage (i)]. The procedures used for  $\text{Na}_2\text{CO}_3$  and calcium acetate were repeated for the removal of excess of acetic acid, and the solid was then dried. Reextraction with *m*-cresol at 353 K for a further period of 24 hr was carried out, the solid being washed several times with *m*-cresol and then with acetone after the *m*-cresol had been decanted off. More attempted extractions produced no decrease in weight of the undissolved solid and no precipitate when the *m*-cresol was poured into diethyl ether (a precipitant for NY). The unextracted residue was dried *in vacuo* for one week at 313 K.

This pure graft copolymer in its acid form was then swollen in a small quantity of methanol. Methylation of the grafts [stage (j)] was effected by means of a solution of diazomethane. The insoluble, partially methylated product was dissolved in dichloroacetic acid and precipitated in diethyl ether. Methylation was repeated until no further effervescence was detected on addition of diazomethane solution to the power swollen in methanol. The pure methylated copolymer, NY/PMA, was finally dissolved in dichloroacetic acid, precipitated in diethyl ether, and dried *in vacuo* at 313 K.

All the *m*-cresol extracts and washings were combined and poured into a large excess of chilled ether [stage (k)] to give the total yield of ungrafted NY as a white powder, which was dried *in vacuo* at 313 K. Microtitrimetry<sup>2</sup> confirmed that no copolymer had been coextracted with the ungrafted NY, and combustion analysis showed that the chemical composition of the ungrafted NY was identical with that of the initial NY prior to irradiation. Microtitrimetry also showed that the methylations in stages (d) and (j) had proceeded to more than 99%.

In order to minimize losses due to transference, chemical reactions and extractions relating to obtaining the pure copolymer were all conducted in one centrifuge tube.

Since preliminary work had shown the true degree of grafting to be low, it was necessary to carry out the irradiation (stage a) on a large quantity of NY (~0.01 kg corresponding to about 100 films) in order to obtain sufficient graft copolymer for subsequent characterization via light scattering. Accordingly, ~ five films were placed in each of five ampoules. The ampoules were irradiated after they had been placed in a holder, the five holes of which corresponded to equal dose rates. The whole procedure was repeated separately three times. The alter-

native expedient of irradiating the 100 films together in one very large ampoule would not have resulted in a uniform absorbed dose throughout the NY.

### Characterization

Experimental procedures used for viscometry, light scattering, and differential refractometry have been described elsewhere.<sup>1,3</sup>

## RESULTS

### Degree of Grafting

Let  $m_0$  = weight of initial NY,  $m$  = weight of grafted film,  $m_e$  = weight of pure copolymer after removal of ungrafted NY. Then, weight of grafts =  $(m - m_0)$  and apparent % grafting =  $100(m - m_0)/m_0$ . Also, weight of NY in pure copolymer =  $m_e - (m - m_0)$ , and hence true % grafting =  $100(m - m_0)/[m_e - (m - m_0)]$ . The apparent and true percentages of grafting were found to be 16.6 and 115%, respectively.

### Isolated Grafts

The PMA produced in stage d was dissolved in 2-butanone. Light scattering at 303 K yielded  $M_{\text{PMA}} = 2.25 \times 10^5$ .

### Initial, Ungrafted, and Grafted Nylon

The initial NY prior to stage a was characterized by light scattering in a ternary solvent<sup>4</sup> of LiCl/TFP/water, yielding a molecular weight of  $49.7 \times 10^3$ . Intrinsic viscosity in *m*-cresol at 298 K, in conjunction with a slightly modified form<sup>2</sup> of the Mark-Houwink relationship quoted by Tuzar et al.,<sup>4</sup> afforded a molecular weight of  $53.7 \times 10^3$ . Similarly, the intrinsic viscosity of ungrafted NY isolated in stage k yielded a molecular weight of  $31.0 \times 10^3$ . The mass of this material relative to that of the initial NY represents  $\bar{W}_u$ , the weight fraction of ungrafted NY.  $\bar{W}_u$  was found to be 0.66. The molecular weight ( $M_{\text{NY}}$ ) of the grafted NY chains in the copolymer was calculated from the following expression, which has been derived previously<sup>2</sup>:

$$M_{\text{NY}} = [(M_P^a - \bar{W}_u M_u^a)/(1 - \bar{W}_u)]^{1/a}$$

Here,  $M_P$  and  $M_u$  relate to the initial and ungrafted NY, respectively, and  $a(=0.732)$  is the exponent in the Mark-Houwink relationship. By this means a value of  $1.06 \times 10^5$  is obtained for  $M_{\text{NY}}$ .

### Composition of Copolymer

This is expressed as the weight fraction  $W_{\text{NY}}$  of the NY in the NY/PMA copolymer. Three methods were used to determine  $W_{\text{NY}}$ , viz., (1) combustion analysis, (2) specific refractive index increment at constant composition in TFP, and (3) specific refractive index increment at constant chemical potential in a TFP/OCF mixture comprising 27% (vol) of TFP. The mean value obtained for  $W_{\text{NY}}$  was 0.42.

### Molar Masses of Copolymer and its Constituents

The difficulties in obtaining a suitable solvent for the copolymer have been discussed in a previous communication,<sup>1</sup> where it was concluded that the most suitable solvents are TFP/OCP mixtures. The copolymer, NY, and PMA are soluble for all values of  $\phi_{\text{TFP}}$  (where  $\phi$  denotes volume fraction in the binary solvent). Moreover, since the refractive indices of TFP and OCP are widely different, it is possible to change the specific refractive index increment ( $\nu$ ) of copolymer or polymer by altering the value of  $\phi_{\text{TFP}}$ , i.e., the composition of the binary solvent. The use of at least three different (pure or mixed) solvents to obtain at least three different specific refractive index increments is necessary when characterizing a copolymer by light scattering.<sup>5-9</sup> This is a consequence of compositional heterogeneity in the copolymer, the measured molar mass of which is an apparent value  $M_c^*$ . The magnitudes of heterogeneity parameters  $P$  and  $Q$  dictate the extent to which  $M_c^*$  differs from the true molar mass  $M_c$ .

It has been demonstrated<sup>6</sup> that the original expressions of Bushuk and Bonoit<sup>5</sup> remain valid, provided that one uses the specific refractive index increments at constant chemical potential ( $\mu$ ) of diffusible low-molecular-weight solvent species. These increments are denoted by  $\nu_\mu$  and are measured after attainment of dialysis equilibrium between polymer solution and binary solvent. The appropriate equivalent expressions become

$$M_c^* = (1/\nu_{\mu c}^2) [\nu_{\mu \text{NY}} \nu_{\mu \text{PMA}} M_c + \nu_{\mu \text{NY}} (\nu_{\mu \text{NY}} - \nu_{\mu \text{PMA}}) W_{\text{NY}} M_{\text{NY}}(\text{domain}) - \nu_{\mu \text{PMA}} (\nu_{\mu \text{NY}} - \nu_{\mu \text{PMA}}) (1 - W_{\text{NY}}) M_{\text{PMA}}(\text{domain})] \quad (1)$$

$$M_c^* = M_c + 2P(\nu_{\mu \text{NY}} - \nu_{\mu \text{PMA}})/\nu_{\mu c} + Q(\nu_{\mu \text{NY}} - \nu_{\mu \text{PMA}})^2/\nu_{\mu c}^2 \quad (2)$$

Light scattering measurements on the NY/PMA copolymer were made using four separate solvent mixtures having  $\phi_1 = 0.27, 0.30, 0.50,$  and  $0.90$ . The Zimm plots afforded four different values of  $M_c^*$ . For each system the value of  $\nu_{\mu c}$  for the copolymer was calculated from the known values<sup>1</sup> of  $\nu_{\mu \text{NY}}$  and  $\nu_{\mu \text{PMA}}$  in conjunction with the value of  $W_{\text{NY}}$ . This assumes that  $\nu_{\mu c}$  is a linear weighted sum of  $\nu_{\mu \text{NY}}$  and  $\nu_{\mu \text{PMA}}$ . Although such a procedure is invariably valid for  $\nu$  at constant composition, it may not be so for  $\nu$  at constant chemical potential.<sup>10</sup> In the present instance however, the assumption appears justified in view of the fact that  $W_{\text{NY}}$  calculated on the basis of a linear weighted sum was found to agree very well with  $W_{\text{NY}}$  evaluated by independent means.

The results relating to solutions of  $\phi_1 = 0.30, 0.50,$  and  $0.90$  were applied to eqs. (1) and (2). Solutions of the sets of simultaneous equations yielded  $M_c = 3.23 \times 10^6$ ,  $M_{\text{NY}}(\text{domain}) = 7.70 \times 10^5$ ,  $M_{\text{PMA}}(\text{domain}) = 3.77 \times 10^6$ ,  $P/M_c = -0.17$ , and  $Q/M_c = 0.06$ .

The variation of  $M_c^*$  with  $(\nu_{\mu \text{NY}} - \nu_{\mu \text{PMA}})/\nu_{\mu c}$  for all four binary solvent systems is shown in Figure 2, which reveals the parabolic form demanded by eqs. (1) and (2). These equations show<sup>9</sup> that when the abscissa has a value of zero, the corresponding value of the ordinate should be  $M_c$ . Extrapolation to this condition is indicated, and the resultant value of  $M_c$ . Extrapolation to this condition is indicated, and the resultant value of  $M_c$  ( $= 3.3 \times 10^6$ ) lies in excellent accord with  $M_c$  obtained via simultaneous equations. Another feature of eqs. (1) and (2) is that, when the abscissa equals  $1/W_{\text{NY}}$ , the ordinate has a value of  $M_{\text{NY}}(\text{domain})/W_{\text{NY}}$ . Actually, it is unnecessary to invoke the parabola in order to evaluate  $M_{\text{NY}}(\text{domain})$  via these coordinates in the present instance, since they

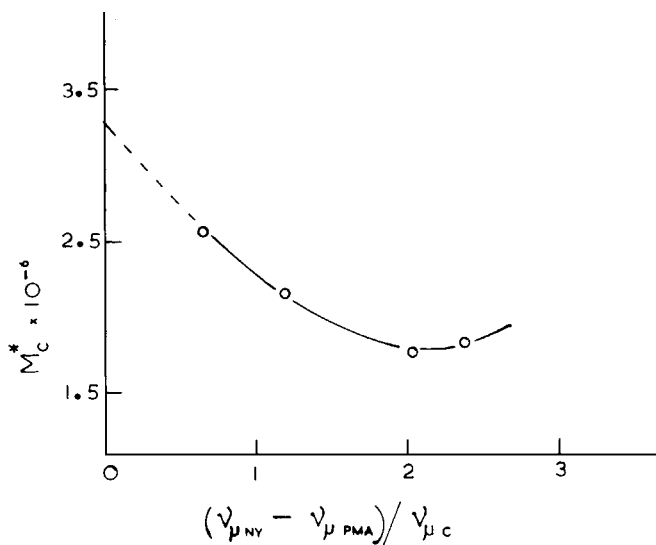


Fig. 2. Plot of apparent molar mass of methylated pure copolymer measured in mixed solvents versus  $(\nu_{\mu_{NY}} - \nu_{\mu_{PMA}})/\nu_{\mu_c}$ .

arise simply by setting  $\nu_{\mu_{PMA}} = 0$  in eq. (1). The binary solvent of  $\phi_{TFP} = 0.27$  fulfills this condition and was selected because of its ability to optically mask the PMA portion of the copolymer.<sup>1</sup> Consequently, the value of  $M_c^*$  obtained in this solvent affords  $M_{NY}(\text{domain})$  from the following form of eq. (1):

$$M_c^* = (\nu_{\mu_{NY}}/\nu_{\mu_c})^2 W_{NY} M_{NY}(\text{domain}) \quad (3)$$

When  $\nu_{\mu_{PMA}} = 0$ , eq. (3) reduces to

$$M_c^* = M_{NY}(\text{domain})/W_{NY}$$

The resultant value of  $M_{NY}(\text{domain})$  is  $7.64 \times 10^5$ , which is in very good accord with the value of  $7.70 \times 10^5$  obtained via simultaneous equations. For a copolymer or a mixture, the molecular weight is respectively greater than or equal to the weighted sum of the molecular weights of the constituents<sup>9</sup>:

$$M_c \geq W_{NY} M_{NY}(\text{domain}) + (1 - W_{NY}) M_{PMA}(\text{domain}) \quad (4)$$

Insertion of the experimentally found values confirms the expected inequality for a copolymer, i.e., the left-hand side of eq. (4) is greater than the right-hand side ( $3.2 \times 10^6 > 2.5 \times 10^6$ ).

Finally, an estimate is made of the number of chains ( $n$ ) of each component within the copolymer molecule:

$$\begin{aligned} n_{NY} &= M_{NY}(\text{domain})/M_{NY} = 7.3 \\ n_{PMA} &= M_{PMA}(\text{domain})/M_{PMA} = 16.7 \end{aligned}$$

## DISCUSSION

In view of the consistency already referred to with respect to  $M_c$  and  $M_{NY}(\text{domain})$ , considerable reliance is placed on the molar masses. The composition of the copolymer was determined to be  $W_{NY} = 0.42$  via three different methods.

Additional corroboration is evident when  $W_{\text{NY}}$  is obtained by calculation. Thus, the pure copolymer NY/PAA has a degree of grafting of 115%. After methylation the grafts increase in weight by a factor 86/72, and the degree of grafting in pure NY/PMA is thus  $115(86/72) = 137.4\%$ . Hence, the composition is given as  $W_{\text{NY}} = 100/(100 + 137.4) = 0.42$ .

By definition,<sup>9</sup> the parameters  $P$  and  $Q$  should lie within the intervals

$$-W_{\text{NY}}M_c \leq P \leq (1 - W_{\text{NY}})M_c \quad (5)$$

$$0 \leq (Q/M_c) \leq W_{\text{NY}}(1 - W_{\text{NY}}) \quad (6)$$

$P$  is a measure of the tendency of copolymer composition to change with  $M_c$ . The deviation in composition of copolymer molecules from the average (analytical) one is characterized by  $Q/M_c$ . A maximum value of  $Q/M_c$  holds for a mixture of homopolymers having the same composition and molar mass as the copolymer.<sup>5,11</sup> Hence, the value of  $Q/Q_{\text{max}}$  can serve as a quantitative measure of the compositional heterogeneity of the copolymer.

Theoretical expressions have been formulated<sup>12,13</sup> for  $P$  and  $Q$  applicable to model copolymers, but unfortunately all systems are simplified and bear little relation to the complex structure, which apparently obtains in the NY/PMA copolymer. Consequently, we have attempted no comparison with predictions for theoretical models. Of equal importance is the confidence that can be placed in the experimentally determined values of  $P$  and  $Q$ . Vorlíček and Kratochvíl<sup>14</sup> concluded that for  $Q/M_c < 10\%$  of the maximum attainable it is necessary that  $M_c$  be at least  $5 \times 10^5$  for reasonable accuracy in determining  $Q$ . Moreover, they demonstrated that  $Q/M_c$  decreases rapidly when the copolymer molecule contains more than one or two grafts. The present copolymer is of sufficiently high molar mass for reasonable confidence to be placed in the values of  $P$  and  $Q$ . The maximum value of  $Q/M_c$  obtainable for this copolymer is  $W_{\text{NY}}(1 - W_{\text{NY}}) = 0.244$ . As the actual value is 0.06, the ratio  $Q/Q_{\text{max}}$  equals 0.246, and it is concluded that the copolymer is moderately heterogeneous with respect to composition. Without fractionation of the copolymer with respect to molecular weight and investigation into whether there is concomitant fractionation with respect to composition, we cannot comment on the value obtained for  $P/M_c$ . It should be noted however, that the negative value is quite consistent with the possible theoretical range [eq. (5)].

Although the overall grafting frequency is  $(16.7/7.3) \approx 2$ , this value is compatible with very many possible structures.<sup>2</sup> Here a simple picture of two pendant PAA grafts per NY backbone is clearly untenable. In order for the NY/PMA molecule to accommodate several chains of each constituent (NY and PMA), the NY chains must be linked. It is not possible to assign a definite structure, but certain relevant pointers are discussed as follows:

(1) Magat et al.<sup>15</sup> have demonstrated a marked difference between the actual number of grafting loci and the number calculated from the absorbed dose and the  $G(\text{radical})$  value of the nylon (nylon 6,6 was used). A value of  $3 \text{ heV}^{-1}$  ( $1 \text{ heV} = 100 \text{ eV} = 1.602 \times 10^{-17} \text{ J}$ ) was taken for  $G(\text{radical})$ , and the actual number of radical sites was obtained via the expedient of using a monomer which does not homopolymerize (maleic acid). The number of grafts is thus half the number of titrateable carboxyl groups. It was found that each radical initiates a graft followed, on average, by seven additional transfer reactions during the kinetic chain. The discrepancy between calculated and actual number of grafting loci

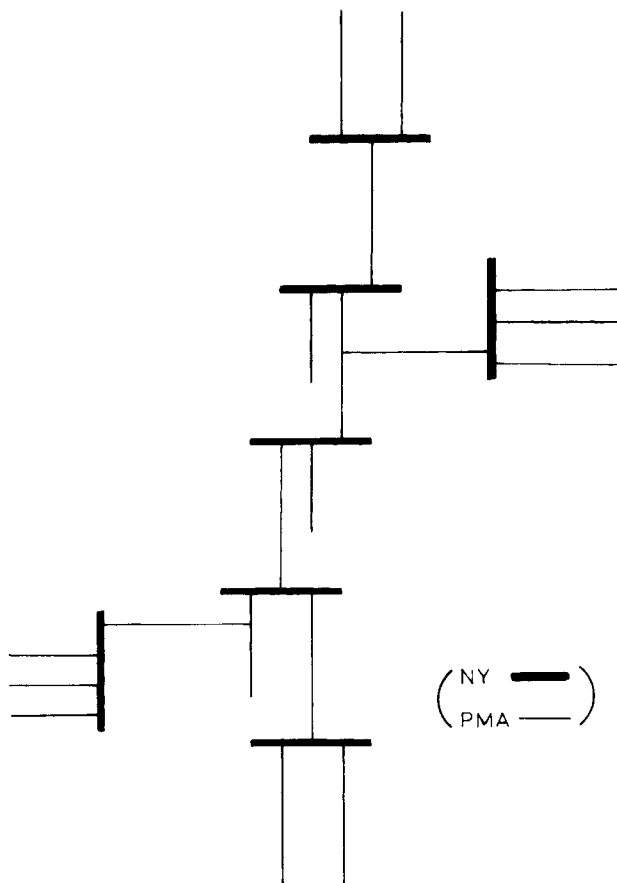


Fig. 3. A possible form of the branched copolymer comprising 7 chains of NY and 17 chains of PMA.

in this system becomes even greater if one uses a more recent value<sup>16</sup> of  $1.0 \text{ heV}^{-1}$  for  $G(\text{radical})$ .

(2) When the latter value of  $G(\text{radical})$  is used in conjunction with the absorbed dose and a molar mass  $M_{\text{NY}} = 10^5$  in the present system, it emerges that the calculated number of grafting loci per NY chain in the copolymer is less than unity (actually  $\sim 0.1$ ). Hence, the situation discussed in (1) above is very likely to apply here, and also there is the strong possibility of linking between NY chains.

(3) A simplified kinetic analysis has shown<sup>17</sup> that during grafting, bimolecular termination occurs in addition to termination by cupric ions. If all, or even part, of this bimolecular termination of growing PAA proceeds by combination, then individual grafts will join and thus link the NY backbones via combined PAA grafts.

(4) We have demonstrated previously<sup>18</sup> that during the homopolymerization of AA in aqueous solution in the presence of  $\text{CuCl}_2$  chain transfer to polymer is a significant process; it doubtlessly occurs also from growing grafts. Chain transfer can thus generate radical sites on PAA chains which have terminated bimolecularly. Grafting from these sites (i.e., grafting to grafts) can also produce PAA capable of bimolecular termination.



(5) It appears, therefore, that the copolymer has a highly branched structure. Supporting evidence is provided by the intrinsic viscosities of the initial NY and the copolymer in TFP. The values of  $[\eta]$  are, respectively, 185 and 55 dm<sup>3</sup>/kg. Although the copolymer comprises only 42 wt % of NY, this is still a remarkable difference in view of the fact that the molar mass of the copolymer is 60 times greater than that of the initial NY. It is well documented<sup>19</sup> that branched structures can be reflected in such large differences in  $[\eta]$ . A branched structure of the NY/PMA molecule is given in Figure 3. This is not, of course, intended to represent the actual structure but merely serves to clarify the points discussed in items (1) through (5).

The question arises as to whether a molecule of such a form would be soluble. Perhaps the most suitable examples of common, high-molecular-weight branched macromolecules are the naturally occurring polysaccharides dextran, amylopectin, and glycogen. Typically, these materials have up to 12% branching and molar masses of 10<sup>6</sup>–(400 × 10<sup>6</sup>). All are soluble in water,<sup>20</sup> the solubility being promoted by hydrogen bond formation between the solvent and hydroxyl groups of the polysaccharides. Such specific interactions can certainly account for the solubility of NY/PMA in TFP/OCP mixtures. As shown by infrared analysis both components of the binary solvent are strongly hydrogen bonding and are thus able to interact with carbonyl groups in both NY and PMA as well as the amide group present in NY.

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